

## CATALYTIC GASIFICATION OF LIGNITE CHARs

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### INTRODUCTION

In a previous study (1), the kinetics of the gasification of chars derived from coals ranging from anthracite to lignite were determined in different gasification media. The relative reactivity factor decreased systematically with increasing carbon content in the parent coal. The overall decrease is caused both by decreasing surface areas and by decreasing specific surface reactivities of the chars. The correlations developed, however, do not generally apply to the lignite chars because of catalytic effects of exchangeable cations, particularly sodium and calcium, which are associated with the carboxyl groups of the lignites. Therefore, a systematic investigation was conducted to obtain detailed data describing the gasification characteristics of Montana and North Dakota lignite chars with particular emphasis given to determining the effect of sodium and calcium inherent or added by base exchange on the gasification rate. Calcium and sodium were chosen because these are the predominant exchangeable cations present in Montana and North Dakota lignites.

### APPARATUS AND EXPERIMENTAL PROCEDURE

A high-pressure thermobalance was used in this work to obtain reaction rates. The main feature of this apparatus is that the weight of a small fixed-bed sample of char (approximately 0.5 gram) contained in a wire mesh basket can be continuously measured as it undergoes gasification in a desired environment at constant temperature and pressure. In all of the tests conducted, chars in -20+40 USS sieve size particles were used, and gas flow rates in the reactor were maintained at sufficiently high values to result in negligible gas conversion. The weight loss versus time characteristics obtained during individual tests were used to calculate the base carbon conversion fraction (1).

The proximate and ultimate analyses of the lignite samples are shown in Table 1. The acid-washed lignites were prepared from the original lignites by treatment with 1N HCl at room temperature followed by washing with distilled water until the effluents were chloride free. The wet samples were dried at 60°C under vacuum. The acid-washed lignites were treated, in turn, with solutions of sodium or calcium acetate, and a number of lignite samples of varying concentrations of base exchanged sodium and calcium were prepared. The nomenclature of the original and treated lignites, together with the concentration of sodium and calcium, is given in Table 2. Chars were prepared from samples by devolatilization in nitrogen (1 atmosphere) for 30 minutes at temperatures from 1400° to 1700°F. For these samples, devolatilization was essentially complete at the lowest temperature used, and the concentration of sodium and/or calcium for chars from the same starting lignite was assumed to be the same at different char preparation temperatures.

Gasification of the chars was conducted at the char preparation temperatures with hydrogen and equimolar steam-hydrogen mixtures at pressures ranging from 14.6 to 69.0 atmospheres. With one sample (G), gasification was conducted in synthesis gas mixtures. The compositions of the synthesis gas mixtures are shown in Table 3.

Table 1. ANALYSES OF LIGNITES

Sample	Proximate Analysis			Ultimate Analysis					
	VM	FC	Ash	C	H	O	N	S	Ash
	wt % dry			wt % dry					
Montana, Raw	43.6	51.3	5.1	65.13	4.13	24.20	0.89	0.57	5.08
Montana, Acid Washed	46.9	52.1	1.0	68.60	4.42	24.57	0.90	0.58	1.00
North Dakota, Raw	43.7	49.6	6.7	62.90	4.27	24.09	0.97	1.10	6.67
North Dakota, Acid Washed	45.8	52.5	1.7	67.70	4.33	24.38	1.00	0.90	1.69

Table 2. NOMENCLATURE OF THE SAMPLES AND THEIR SODIUM AND CALCIUM CONTENT

No.	Sample	Name	Concentration, g-atoms/g-atom base carbon		
			Na	Ca	Na + Ca
1.	Montana, Acid Washed	A	0.00000	0.00000	0.00000
2.	Montana, Ca-Ex. 1	B	0.00000	0.00139	0.00139
3.	Montana, Ca-Ex. 2	C	0.00000	0.00972	0.00972
4.	Montana, Raw	D	0.00164	0.01364	0.01528
5.	Montana, Na+Ca-Ex	E	0.01098	0.00505	0.01603
6.	Montana, Na-Ex. 1	F	0.00274	0.00000	0.00274
7.	Montana, Na-Ex. 2	G	0.01955	0.00000	0.01955
8.	North Dakota, Raw	N	0.00329	0.00758	0.01087
9.	North Dakota, Acid Washed	O	0.00000	0.00000	0.00000
10.	North Dakota, Ca-Ex	P	0.00000	0.01326	0.01326

Table 3. COMPOSITION OF SYNTHESIS GAS MIXTURES

	<u>H<sub>2</sub></u>	<u>H<sub>2</sub>O</u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>CH<sub>4</sub></u>
	vol %				
Syn-Gas 1	47.5	40.4	6.0	3.6	2.5
Syn-Gas 2	43.6	35.3	11.8	8.2	1.1
Syn-Gas 3	36.8	29.3	19.3	11.3	3.3

## RESULTS AND DISCUSSION

### Gasification in Hydrogen

Initial gasification tests in hydrogen were conducted with Montana and North Dakota chars obtained from acid-treated lignites to provide a basis for determining gasification kinetics in the absence of exchangeable cations. Typical results are shown in Figures 1 and 2. The results show that, at a given temperature, gasification rates increased significantly with increasing hydrogen pressure. Similarly, at a constant hydrogen pressure, gasification rates increase significantly with increasing temperature. For Montana char, a carbon conversion of approximately 0.09, which tends to be independent of temperature and pressure, occurred during the heat-up period of char (which takes about 1 to 2 minutes after lowering the sample to the reaction zone). It was hypothesized that Montana chars contain two types of carbon - Type I, which gasifies very rapidly during the heat-up period, and Type II, which is subsequently gasified. For North Dakota chars, only Type II carbon was indicated.

In previous studies (2) with bituminous coal chars, gasification kinetics in hydrogen was described by the expression --

$$\frac{dX}{dt} = f_L K_H (1-X) \quad 1)$$

where --

$X$  = base carbon fraction

$t$  = time, min

$K_H$  = rate constant for reference char ( $f_L = 1$ ),  $\text{min}^{-1}$ .

The rate constant was determined by the equation --

$$K_H = \frac{P_{H_2}^2 \exp (2.674 - 24,609/T)}{1 + P_{H_2} \exp (-10.452 + 19.976/T)} \quad 2)$$

where --

$f_L$  = relative reactivity factor

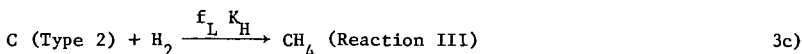
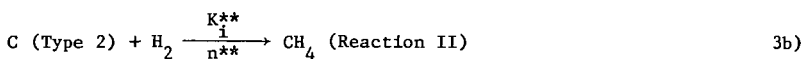
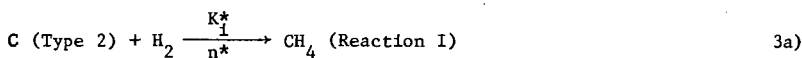
$T$  = temperature, °R

$P_{H_2}$  = hydrogen partial pressure, atm.

Figure 3 shows the  $-\ln(1-X)$  versus reaction time plots for the experimental results of gasification in hydrogen for Montana lignite chars. Also included in the figure is the calculated base carbon conversion fraction for the reference bituminous coal char (char from preoxidized Pittsburgh No. 8 seam coal). The experimental base carbon conversion data for Montana lignite are nonlinear when plotted according to Equation 1. The curve for the char from Raw Montana starts with a high initial slope; however, the value of the slope decreases with the increase of  $X$  and, at high value of  $X$ , becomes lower than that for the reference bituminous char. Upon removal of exchangeable cations, the reactivity of char decreases and the extent of nonlinearity is diminished but not entirely removed.

To take into account the characteristics of lignite char gasification mentioned above, it has been assumed that there are two transient reactions in addition to the low-rate gasification reactions that determine the rate of lignite char gasification. The first transient reaction is assumed to be catalyzed by some structural component present in lignite char, and the second transient reaction is assumed to be catalyzed by the exchangeable cations present in lignite. It is also assumed that the low-rate gasification of lignite char is kinetically similar to the low-rate gasification occurring in bituminous coal char.

The following reaction model was proposed: The Montana lignite char is composed of two types of carbon. In the presence of hydrogen, a fraction of carbon (Type 1) is gasified very rapidly to methane during the heat-up period (1 to 2 minutes in thermobalance tests). The remaining carbon (Type 2) gasifies by three possible paths, as indicated below:



Reaction III is assumed to be similar to the reaction path followed by bituminous coal char (low-rate gasification). The parameters  $f_L$  and  $K_H$  have been defined (2). Reaction I corresponds to a path in which some entity,  $n^*$ , catalyzes gasification. The entity  $n^*$  is assumed to be a structural component present in char. It is also assumed that  $n^*$  deactivates by a first-order process. For Reaction II,  $n^{**}$  is a metal, catalyst-containing complex that catalyzes this reaction. Similar to Reaction I, it was assumed that  $n^{**}$  also deactivates by a first-order process.

With the above assumptions, the following rate expression results -

$$-\ln(1-X) = -\ln(1-X^*) + \frac{K_1^* C_O}{K^*} (1 - e^{-\frac{K_1^* t}{K^*}}) + \frac{K_1^{**} C_O}{K^{**}} (1 - e^{-\frac{K_1^{**} t}{K^{**}}}) + f_L K_H t \quad 4)$$

The different parameters of Equation 4 were evaluated from experimental data. For chars from both lignites -

$$K^* = K^{**} = 5.74 \exp(-9770/T) \quad 5)$$

Particular evaluations for chars from Montana lignite are the following:

$$f_L = 0.70$$

$$X^* = 0.086$$

$$\frac{K_1^* C_O}{K^*} = 0.026 P_{H_2}^{1/2}$$

$$\frac{K_1^{**} C_{Na}}{K^{**}} = (380 C_{Na} + 32 C_{Ca}) f_L K_H \quad 6)$$

where  $C_{Na}$  and  $C_{Ca}$  are concentrations of sodium and calcium, g-atom/g-atom base carbon.

Equation 4 was used with the evaluation given above to calculate the base carbon conversion for the chars from Raw Montana lignite. In Figure 4, the solid line represents the calculated values of X. The experimental points shown follow the line closely except for the first 5 minutes of reaction time. A similar match was obtained for the other char samples.

Particular evaluations for chars from North Dakota lignite are the following:

$$f_L = 0.85$$

$$X^* = 0.0$$

$$\frac{K^*C_o}{K_o} = 0.045 P_{H_2}^{1/2}$$

$$K^{**}C_{1n}^{*o} = (500C_{Na} + 75C_{Ca}) f_L K_H \quad 7)$$

The evaluation of the term  $K^{**}C_{1n}^{*o}$ , in terms of catalyst concentration show that, for both lignites, sodium was a better catalyst than calcium for hydrogasification. This observation can also be verified by choosing the time for 50% ( $T_{0.5}$ ) carbon conversion as a rate parameter. The time to reach a certain fraction of carbon conversion is a measure of reaction rate even for a reaction which is not first-order (3). The  $T_{0.5}$  values are presented in Table 4 for different chars obtained from Montana lignite. The  $1/T_{0.5}$  values of the chars containing only sodium or only calcium are shown in Figure 5, plotted against the concentration of Na or Ca. The values for the acid-washed lignite chars are also shown. It is clear that calcium is a poor catalyst for hydrogasification.

Table 4. TIME FOR 50% BASE CARBON CONVERSION OF MONTANA CHARs

Sample	Reaction Temperature, °F	Hydrogen Pressure, atm	$T_{0.5}$ , min (time for X=0.5)	$\frac{1}{T_{0.5}}$ , min <sup>-1</sup>
A	1600	35	100.0	0.0100
A	1700	35	39.0	0.0256
A	1600	69	44.0	0.0227
A	1700	69	18.5	0.0540
B	1600	35	105.0	0.0095
B	1700	35	34.0	0.0294
C	1600	35	100.0	0.0100
C	1700	35	31.0	0.0322
D	1600	35	78.0	0.0128
D	1700	35	26.5	0.0377
E	1600	35	48.5	0.0206
E	1700	35	19.0	0.0526
E	1600	69	11.8	0.0847
E	1700	69	4.5	0.2222
F	1600	35	68.0	0.0147
F	1700	35	23.5	0.0425
G	1600	35	20.5	0.0488
G	1700	35	9.0	0.1111

### Gasification in Equimolar Steam-Hydrogen Mixtures:

Gasification in equimolar steam-hydrogen mixtures was conducted with different char samples at temperatures of 1500° to 1700°F and at pressures of 14.6 to 69.0 atmospheres. The effect of total pressure on gasification for char, obtained from acid-washed North Dakota lignite is shown in Figure 6. The rate of gasification increased with the increase of total pressure. These results were anticipated because at higher total pressure, the partial pressure of hydrogen will be higher; that alone could enhance the rate of gasification, even if the rate was independent of steam partial pressure. In contrast, it was observed that, for samples containing Na or Ca, the gasification rate in this medium was independent of total pressure. Typical results indicating this behavior are presented in Figure 7. In this context, Vadovic and Eakman (4) have shown that for steam gasification of chars catalyzed by potassium, the rate was independent of steam partial pressure. The results of the current investigation indicate that, for chars containing Na or Ca as catalyst, the gasification rate is controlled by the steam-carbon reaction, even though the gasification medium contains 50% hydrogen. For all of the char samples, the rate of gasification in equimolar steam-hydrogen mixtures increased with temperature. Typical gasification data for chars containing different amounts of catalyst are shown in Figure 8.

It has been shown (2) that, with bituminous coal chars, gasification in steam-hydrogen mixtures could be correlated by the expression -

$$\frac{dX}{dt} = f_L K_T (1-X)^{2/3} \exp(-\alpha X^2) \quad (8)$$

Integrating Equation 8, we obtain -

$$M(X) = \int_0^X \frac{\exp(\alpha X^2)}{(1-X)^{2/3}} = f_L K_T + I \quad (9)$$

where -

$K_T$  = overall rate constant

$f_L$  = relative reactivity factor

$\alpha$  = kinetic parameter dependent on gas composition

$I$  = integration constant.

For bituminous coal chars, which were devolatilized at temperatures of 1400°F or higher,  $I = 0.0$ , and  $\alpha$ , for equimolar steam-hydrogen mixtures, is equal to 1.67. The char gasification data of this study was analyzed by Equation 9 assuming  $\alpha$  to be equal to 1.67. Typical plots of  $M(X)$  versus time for three char samples are shown in Figure 9. Linear plots of up to a value of  $X=0.86$  were obtained, but all the lines do not pass through the origin. The acid-washed lignite chars tend to have an intercept of about 0.1. The slope and intercept values of all the chars tested are shown in Table 5. In Figure 10, the values of the overall rate constant ( $f_L K_T$ ) for steam-hydrogen gasification of Montana chars are plotted against the total concentration of sodium and/or calcium present in the char. All of the experimental points, whether the char contained only sodium, only calcium, or their mixture, tended to fall on the same line at a particular temperature, indicating that, in steam-hydrogen mixtures, calcium is as effective a catalyst as sodium. For Montana chars, the increase of rate with the increase of catalyst concentration and temperature can be correlated by the following experimental equation:

$$\text{Overall rate} = f_L K_T = [C_{(\text{Na}+\text{Ca})} + 0.0032]\exp(19.80 - 38000/T) \quad 10)$$

Table 5. KINETIC PARAMETERS FOR GASIFICATION OF CHARs FROM MONTANA AND NORTH DAKOTA LIGNITES IN EQUIMOLAR STEAM-HYDROGEN MIXTURES

Char Source	Temperature, °F	$f_L K_T$ (Slope)	I (Intercept)
A	1500	0.0030	0.10
A	1600	0.0082	0.10
A	1700	0.0262	0.08
B	1500	0.0050	0.10
B	1600	0.0240	0.08
B	1700	0.0473	0.10
C	1600	0.0546	0.05
C	1700	0.1175	0.00
D	1500	0.0235	0.06
D	1600	0.0796	0.00
D	1700	0.1640	0.00
F	1600	0.0340	0.05
F	1700	0.1000	0.00
G	1500	0.0332	0.08
G	1600	0.0954	0.00
G	1700	0.1892	0.00
O	1500	0.0046	0.05
O	1600	0.0136	0.09
O	1700	0.0249	0.08
N	1500	0.0410	0.00
N	1600	0.0972	0.00
N	1700	0.1680	0.00
P	1500	0.0502	0.00
P	1600	0.1050	0.00
P	1700	0.2205	0.00

For North Dakota chars, the following correlations satisfy the experimental results:

$$\text{Overall rate} = f_L K_T = [C_{(\text{Ca}+\text{Na})} + 0.0015]\exp(16.58 - 30000/T) \quad 11)$$

The gasification characteristics of chars from two lignites having similar elemental compositions are qualitatively similar, but, the numerical magnitude of the rate parameters differ. That is, enhancement of rate by a catalyst is dependent upon the nature of the char on which the catalyst is distributed.

#### Gasification in Synthesis Gas Mixtures

Gasification of one sample of char from Montana lignite was conducted in synthesis gas (syn-gas) mixtures. Tests were done with Syn-Gas 2 at 35 and 69 atmospheres at a temperature of 1700°F, and it was noted that the rate of base carbon conversion was the same at both pressures. The effect of pressure on rate of gasification in synthesis gas mixtures seems to be the same as was observed for gasifi-

cation in steam-hydrogen mixtures. The results of gasification with different syn-gas mixtures are shown in Figure 11. The gasification data in equimolar steam-hydrogen mixtures are also shown in this figure. The  $(P_{H_2}/P_{H_2O})$  ratio for the syn-gas mixtures are 1.18, 1.23, and 1.25 for the three mixtures shown in Table 3. The  $(P_{CO}/P_{H_2O})$  ratios are 0.15, 0.33, and 0.66. Therefore, the main compositional variable between the three synthesis gas mixtures is the  $CO/H_2O$  ratio. The effect of  $CO_2$  and  $CH_4$  in the mixture was considered to be minor. It is seen from Figure 11 that at the same temperature and pressure, the rate of carbon conversion decreases with the increase of the  $CO/H_2O$  ratio. The overall rate constants ( $k_L, K_T$ ) for the gasification in syn-gas was calculated with Equation 9. The values are 0.100, 0.076, and 0.039 respectively, for the three mixtures. It is seen that, for char from Sample G the rate of gasification in equimolar steam-hydrogen mixtures was approximately five times higher compared with that for Syn-Gas 3.

### CONCLUSIONS

For gasification of lignite chars in hydrogen, sodium was more efficient as a catalyst than calcium. The gasification rate of lignite chars containing sodium or calcium remains essentially constant with the increase of total pressure in steam-hydrogen and synthesis gas mixtures. Both calcium and sodium enhance the rate of gasification of lignite chars in steam-hydrogen mixtures, and the effect is proportional to the concentration (g-atom/g-atom carbon) of sodium and/or calcium present. The catalytic effect of sodium or calcium depends on the nature of char on which the catalyst is dispersed; that is, the same concentration of sodium does not produce the same quantitative effect on rate for chars obtained from lignites having similar elemental composition. The catalysts tend to selectively enhance the rate of the steam-carbon reaction, preferring the carbon-hydrogen reaction when gasification is conducted in steam-hydrogen mixtures.

### LITERATURE CITED

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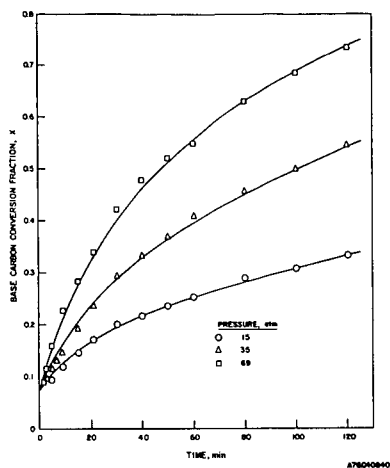


Figure 1. CONVERSION OF ACID-TREATED MONTANA LIGNITE CHAR IN HYDROGEN AT 1600°F

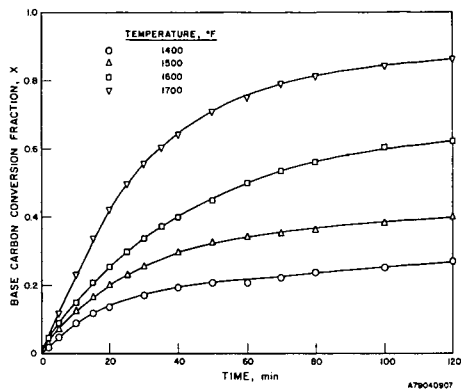


Figure 2. GASIFICATION OF ACID-WASHED NORTH DAKOTA CHARS IN HYDROGEN AT 35 atm

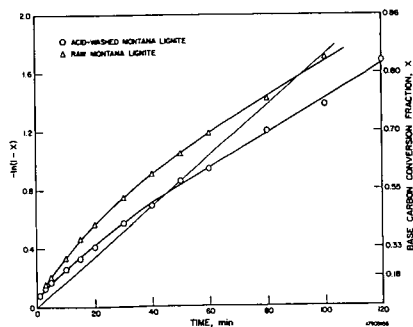


Figure 3. GASIFICATION OF RAW AND ACID-WASHED MONTANA LIGNITE CHARS IN HYDROGEN AT 1700°F AND 35 atm

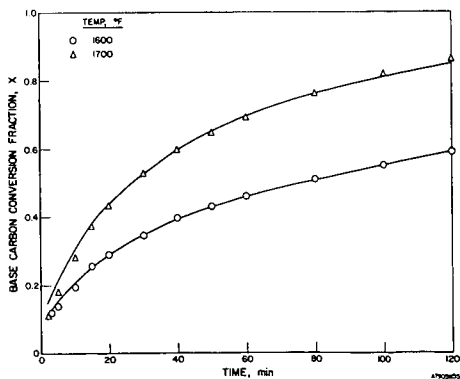


Figure 4. GASIFICATION OF RAW MONTANA CHARS IN HYDROGEN AT 35 atm

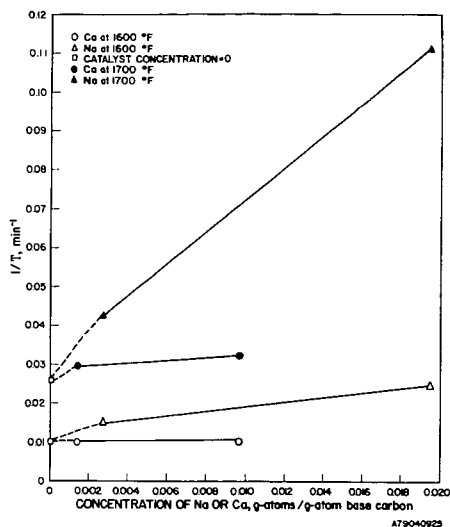


Figure 5. EFFECT OF CATALYST CONCENTRATION ON THE RECIPROCAL TIME FOR 50% BASE CARBON CONVERSION

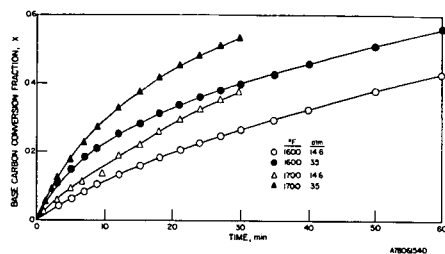


Figure 6. GASIFICATION OF ACID-WASHED NORTH DAKOTA CHARS IN STEAM-HYDROGEN MIXTURES ( $H_2O/H_2 = 1$ )

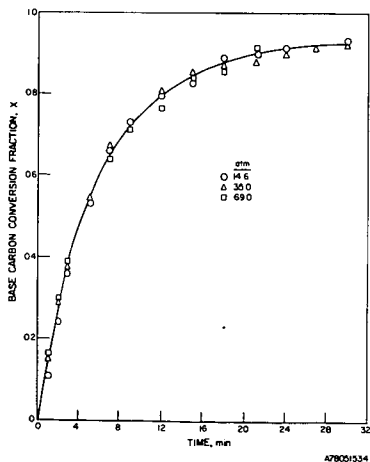


Figure 7. EFFECT OF PRESSURE ON THE GASIFICATION OF NORTH DAKOTA RAW CHAR IN STEAM-HYDROGEN MIXTURES ( $H_2O/H_2=1$ ) AT 1700 °F

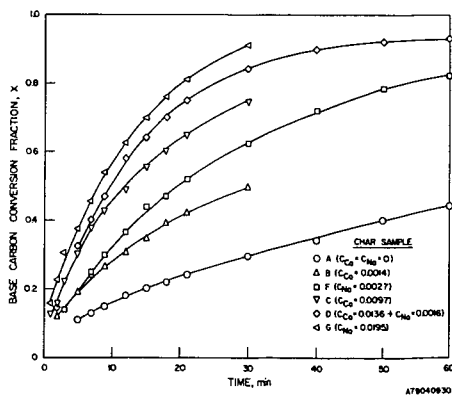


Figure 8. GASIFICATION OF MONTANA CHARS IN EQUIMOLAR STEAM-HYDROGEN MIXTURES AT 1600 °F AND 35 atm

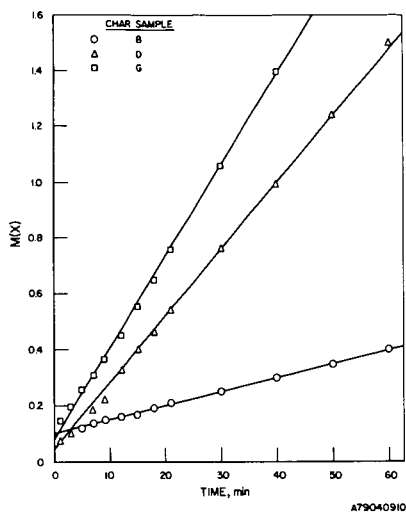


Figure 9. BASE CARBON CONVERSION FUNCTION VS. TIME PLOTS FOR THE GASIFICATION OF MONTANA LIGNITE CHARS IN EQUIMOLAR STEAM-HYDROGEN MIXTURES AT 1500°F AND 35 atm

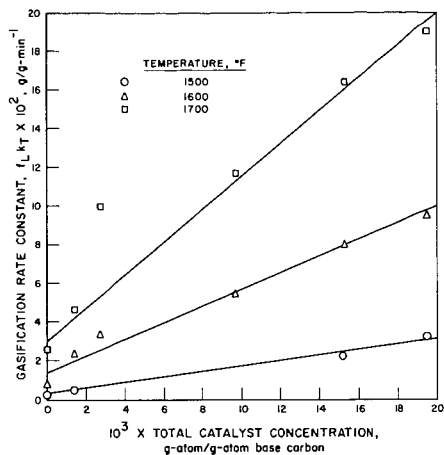


Figure 10. EFFECT OF CATALYST CONCENTRATION ON THE OVERALL RATE OF GASIFICATION OF MONTANA LIGNITE CHARS IN EQUIMOLAR STEAM-HYDROGEN MIXTURES AT A TOTAL PRESSURE OF 35 atm

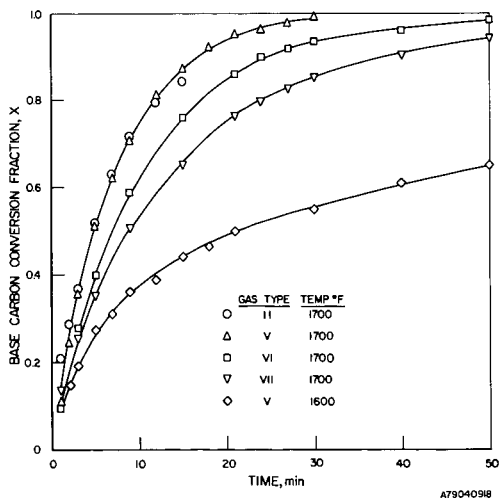


Figure 11. GASIFICATION OF CHARS FROM SAMPLE G IN SYNTHESIS GAS MIXTURES AT 35 atm